

Modeling the partitioning of BTEX in water-reformulated gasoline systems containing ethanol

Stephen E. Heermann, Susan E. Powers *

Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY 13699-5710, USA

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Abstract

The objectives of this research were to quantify the extent of cosolvency for water–gasoline mixtures containing ethanol and to identify appropriate modeling tools for predicting the equilibrium partitioning of BTEX compounds and ethanol between an ethanol-bearing gasoline and water. Batch-equilibrium experiments were performed to measure ethanol and BTEX partitioning between a gasoline and aqueous phase. The experiments incorporated simple binary and multi-component organic mixtures comprised of as many as eight compounds as well as highly complex commercial gasolines where the composition of the organic phase was not completely defined. At high ethanol volume fractions, the measured partition coefficients displayed an approximate linear relationship when plotted on semi-log scale as a function of ethanol volume fraction. At lower concentrations, however, there was a distinctly different trend which is attributed to a change in solubilization mechanisms at these concentrations. Three mathematical models were compared with or fit to the experimental results. Log-linear and UNIFAC-based models were used in a predictive capacity and were capable of representing the overall increase in partition coefficients as a function of increasing ethanol content in the aqueous phase. However, neither of these predicted the observed two-part curve. A piecewise model comprised of a linear relationship for low ethanol volume fractions and a log-linear model for higher concentrations was fit to data for a surrogate gasoline comprised of eight compounds and was then used to predict BTEX concentrations in the aqueous phase equilibrated with three different commercial gasolines. This model was superior to the UNIFAC predictions, especially at the low aqueous ethanol concentrations. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cosolvent; Ethanol; Multicomponent; Solubility; UNIFAC; Gasoline pollution

* Corresponding author. Tel.: +1-315-268-6542; fax: +1-315-268-7636; e-mail: sep@draco.clarkson.edu

1. Introduction

Environmental laws in the United States currently require the addition of oxygenated compounds to gasolines in certain areas of the country experiencing air-quality problems in order to reduce emissions of carbon monoxide and other pollutants from automobiles. The quantity of oxygen that must be added is dependent upon the severity of the air quality problem. ‘Reformulated’ gasolines, containing a minimum of 2% oxygen by weight are most commonly required while ‘oxygenated’ gasolines containing 2.7% or more of oxygen may be required in the winter months for the most problematic urban areas (Freed, 1997).

The chemical oxygenates most commonly added to these ‘reformulated gasolines’ include methyl *tert*-butyl ether (MTBE) and ethanol. Of these, MTBE use exceeds that of ethanol. However, the use of ethanol is expected to increase in the United States due to potential health effects associated with MTBE (Bedard, 1995; Gomez-Taylor et al., 1997) and market forces (New York Times, 1997). In order to meet the fuel mandates, reformulated gasolines must contain 5.5% ethanol by volume and oxygenated fuels must contain 7.4% ethanol.

Ethanol is also added to gasolines as an alternative replacement for petroleum compounds. Automobiles are currently being manufactured that may use fuel containing ethanol fractions as high as 85% (New York Times, 1997). Ethanol is an important gasoline constituent in other countries as well. Most notable of these is Brazil, where gasoline formulations typically include 20% or more ethanol (Fernandes, 1997).

The presence of MTBE, ethanol and other chemical oxygenates in gasolines has prompted concern among scientists and environmental regulators regarding their impact in other environmental compartments, including groundwater (e.g., Zogorski et al., 1996). Oxygenates, especially alcohols, can act as a cosolvent and significantly increase the aqueous solubility of potentially harmful hydrocarbons. In a subsurface gasoline spill scenario, the increased hydrocarbon solubility could increase aquifer degradation and increase the potential for human exposure to these chemicals.

Predicting the interphase mass transfer of hydrophobic organic compounds (HOCs) from gasoline to water requires the quantification of equilibrium concentrations between adjoining phases. This requirement exists because the driving force causing mass transfer to occur arises from a departure from thermodynamic equilibrium. In the absence of a cosolvent, BTEX (benzene, toluene, ethylbenzene and xylenes) compounds and other HOCs in the gasoline phase are generally assumed to follow ideal solution behavior. Thus, Raoult’s law is typically used to predict equilibrium concentrations. This quantification method, however, breaks down when oxygenates are present. Because oxygenates such as ethanol and MTBE are polar in nature, they partition in varying degrees into the water. As they partition, the BTEX solubility in the aqueous phase increases and becomes dependent on the cosolvent concentration.

A number of previous studies have examined the influence of alcohols and ethers on HOC solubility. Some of these studies have utilized single HOCs as surrogates for gasoline, neglecting the complexities associated with multicomponent aspects of this organic phase (Groves, 1988; Mihelcic, 1990; Stephenson, 1992; Peschke and Sandler, 1995; Hellinger and Sandler, 1995). Others focused on the potentially detrimental

hygroscopic nature of oxygenated gasolines in automobile engines. They provide information on the partitioning of 'gasoline,' not individual BTEX compounds (Letcher et al., 1986; Lojkásek et al., 1992), and thus have less utility in environmental applications.

The work by Cline et al. (1991) and Poulsen et al. (1992) provide much more substantial information on the partitioning of BTEX compounds from multicomponent gasolines. Cline et al. (1991) developed partition coefficients for BTEX compounds between real gasolines and water. A small number of the gasolines purchased for these experiments contained low concentrations of MTBE. Methanol and MTBE were the oxygenates added to the PS-6 standard API gasoline in the work of Poulsen et al. (1992). They found that, for a given volume of gasoline, increases in the BTEX concentrations due to a cosolvent effect were balanced by the reduced mass of these species in the gasoline due to the initial presence of the oxygenate. Significant increases in aqueous benzene concentrations were observed only when the volume ratio of gasoline to water was high.

Models for describing the effects of cosolvents on HOC solubilities in environmental systems have been presented by several researchers (e.g., Fu and Luthy, 1986; Groves, 1988; Pinal et al., 1990). These studies generally considered the cosolvent effect where the organic phase was comprised of a single HOC. Gasoline, however, represents a highly complex mixture of organic compounds. Poulsen et al. (1992) applied cosolvent models to describe BTEX partitioning from their experiments with PS-6 gasoline and methanol. The models appeared to provide reasonable predictions of aqueous phase concentrations, although the sparse data set available was not sufficient to adequately verify the accuracy of these models. Thus, the degree to which models developed specifically to predict cosolvency effects can be extended to multicomponent organic mixtures remains to be adequately demonstrated.

The principal objectives of this research were to quantify the extent of cosolvency for water–gasoline mixtures containing ethanol and to identify appropriate modeling tools for predicting thermodynamic equilibria of BTEX compounds partitioning between gasoline and aqueous phases in the presence of ethanol. Batch equilibrium experiments were performed to measure equilibrium concentrations and models were fit and compared to these data both for relatively simple multicomponent mixtures comprised of a few compounds, and for highly complex gasolines where the composition of the organic phase was not completely defined. In addition, model coefficient values are provided so that the methods discussed herein can be applied in a predictive capacity to other environmental applications involving the mass transfer of BTEX compounds from gasoline to an aqueous phase.

2. Background

Thermodynamic equilibrium conditions for the partitioning of solutes between gasoline and the aqueous phase under isothermal conditions can be defined by equating the activity of each species between phases:

$$a_i^w = a_i^o \quad i = 1 \dots n \quad (1a)$$

or:

$$X_i^w \gamma_i^w = X_i^o \gamma_i^o \quad i = 1 \dots n \quad (1b)$$

where a_i^j is the activity of the solute i within a given phase j , superscripts o and w refer to the organic and aqueous phases, respectively, and n is the number of compounds in the system. The activity may be expressed as the quantity $X_i^j \gamma_i^j$ where X_i^j is a mole fraction; γ_i^j is the activity coefficient. Eq. (1b) may be rearranged to calculate the mass concentration, C_i^w , of hydrophobic compound i in water in terms of the activity coefficients, organic phase mole fraction, the molar density of the aqueous phase, ρ_m^w , and the molecular weight of compound i , MW_i :

$$C_i^w = X_i^o \frac{\gamma_i^o}{\gamma_i^w} \rho_m^w MW_i \quad (2)$$

Standard formulation gasolines are generally assumed to be comprised of organic chemicals of sufficiently similar molecular properties that their activity coefficients have values in the neighborhood of unity. If it is further assumed that these compounds dissolve in water at such dilute concentrations that their aqueous-phase activity coefficients remain nearly constant, Raoult's law can generally provide a reasonable estimate of the equilibrium aqueous-phase concentration, C_i^w , in terms of the solubility of the pure liquid solute in water, C_i^{*w} (Mackay et al., 1991):

$$C_i^w = C_i^{*w} X_i^o \quad (3)$$

where $C_i^{*w} = \rho_m^w MW_i / \gamma_i^w$. However, in the presence of an oxygenate, high concentrations of the oxygenate and BTEX species may be present in the aqueous phase. In this case, the BTEX concentrations in the water–cosolvent mixture are no longer constant, but are dependent on the composition of the phase and Raoult's law cannot be used directly for modeling the equilibrium partitioning between oxygenated gasolines and water.

Approaches have been developed to directly estimate HOC concentrations cosolvent–water mixtures based on the cosolvent fraction of the aqueous phase (Yalkowsky et al., 1972; Amidon et al., 1974; Yalkowsky et al., 1975; Williams and Amidon, 1984; Banerjee and Yalkowsky, 1988). Most of these approaches and much of the current understanding of HOC solubility in these mixed aqueous solvents have been developed within the pharmaceutical science field in order to provide tools for predicting the solubilities of non-polar drugs in aqueous solvents. Alternatively, the activity coefficients included in Eq. (2) can be estimated using thermodynamic methods such as UNIFAC (Fredenslund et al., 1975). Methods for both directly estimating solubilities and for estimating activity coefficients are discussed herein.

2.1. Models for directly estimating solubilities in cosolvent mixtures

2.1.1. Log-linear model

Yalkowsky et al. (1972) observed that the aqueous solubility of pharmaceutical drugs in a binary aqueous solvent increases approximately exponentially with linear increases

in the volume fraction of the organic cosolvent. Thus, a linear relationship was established between the log-transformed solubility and the cosolvent volume fraction:

$$\ln C_i^{*m} = \ln C_i^{*w} + \sigma_i f \quad (4)$$

where C_i^{*m} and C_i^{*w} are the mass solubilities of HOC compound i in an aqueous-cosolvent mixture (m) and in pure water (w); f is the volume fraction of the cosolvent in the binary solvent; and σ_i is a constant for a given solute–cosolvent system termed the cosolvency factor.

Further work by Rubino and Yalkowsky (1987) demonstrated that the log solubility could be expressed by a linear combination of the log solubility of the solute in the two pure solvents:

$$\ln C_i^{*m} = (1 - f) \ln C_i^{*w} + f \ln C_i^{*c} \quad (5)$$

where C_i^{*c} is the solubility of compound i in pure cosolvent. Thus, the cosolvency factor, σ_i , can be computed from published compilations of solubility data (e.g., Vershueren, 1983; Mackay et al., 1991) by combining Eqs. (4) and (5):

$$\sigma_i = \ln \frac{C_i^{*c}}{C_i^{*w}} \quad (6)$$

The log-linear relationship between HOC solubility and cosolvent volume fraction (Eq. (5)) can be explained in terms of the molecular surface area model for solubility first proposed by Langmuir (Yalkowsky et al., 1975) and developed further in the 1970s and 1980s, especially pertaining solubility in mixed polar solvents (Amidon et al., 1974, 1975; Yalkowsky et al., 1975; Yalkowsky and Valvani, 1976; Valvani et al., 1976; Rubino and Yalkowsky, 1987). According to this model, the excess free energy associated with the solubilization of an HOC into a solvent is proportional to the relative molecular surface areas across which pairs of polar and/or non-polar structural groups interact. When an HOC such as xylene is dissolved in a polar solvent, the number of interactions between like pairs of nonpolar structural groups is greater in a mixed water–oxygenate solvent than for the HOC in pure water. These interactions result in a reduction in the excess free energy associated with HOC solubilization.

Yalkowsky and Valvani (1976) rationalized that the cosolvent volume fraction was a reasonable measure of its molecular surface area. Accordingly, decreases in the excess free energy of solubilization can be linearly related to increases the volume fraction of the cosolvent. To arrive at the relation expressed in Eq. (5), it must be considered that the logarithm of the activity coefficient is, by definition, a measure of the partial molar excess free energy of mixing for a solute placed in a given solvent. Thus, increases in the volume fraction of cosolvent result in decreases in the logarithm of the activity coefficient and, consequently, the logarithm of the HOC solubility increases in the mixed solvent.

2.1.2. Linear / log-linear model

Deviations from the log-linear cosolvency relationship (Eqs. (4) and (5)) have been observed in a number of studies involving non-polar pharmaceutical drugs (Rubino and Yalkowsky, 1987), as well as HOCs of environmental interest (Morris et al., 1988;

Banerjee and Yalkowsky, 1988; Barker et al., 1991; Poulsen et al., 1992; Kimble and Chin, 1994; Li and Andren, 1994). For short-chained alcohols, Rubino and Yalkowsky (1987) attributed these deviations to structural changes in the alcohol–water solution. More precisely, at low alcohol volume fractions, the alcohol molecules become partially segregated from water via the formation of hydration spheres. At higher fractions, however, hydration is no longer a dominant solubilization process and the HOC has access to both water and cosolvent molecules in approximate proportion to their volume fractions. Based on results of a study of aqueous-ethanol solutions, Grunwald (1984) described the volume within such spheres as being in a state of reduced hydrogen bonding as a result of disruption of the water network by the cosolvent. This would lead to a reduction in the hydrophobic effect and an increase in HOC solubility within these spheres. In contrast, outside of the hydration spheres, hydrogen bonding between water molecules is increased and both ethanol and HOC molecules are largely excluded as a result of the hydrophobic effect.

The influence of these structural changes in a mixed aqueous solvent on HOC solubility was demonstrated by Banerjee and Yalkowsky (1988) using toluene as the HOC and propylene glycol and methanol as aqueous cosolvents. At low volume fractions of the cosolvent, the solubility of toluene was found to increase linearly with increasing cosolvent volume fraction while at higher cosolvent fractions, a log-linear relationship was observed. The linear relationship was attributed to a linear increase in the hydration-sphere volume with cosolvent volume fraction. Accordingly, as the volumes of the hydration spheres expand, they intersect and eventually encompass the entire aqueous phase. The authors postulate that the hydration spheres have completely merged at the cosolvent volume fraction coinciding with the breakpoint observed between linear and log-linear relationships.

By incorporating the observed linear relation at lower cosolvent concentrations and the log-linear relation at higher cosolvent concentrations, two equations can be written in piecewise manner to reflect differences in solubilization mechanisms (Banerjee and Yalkowsky, 1988):

$$C_i^{*m} = \left(1 - \frac{f}{\beta}\right) C_i^{*w} + \frac{f}{\beta} C_i^{*\beta} \quad f < \beta \quad (7a)$$

$$\ln C_i^{*m} = \left(1 - \frac{f - \beta}{1 - \beta}\right) \ln C_i^{*\beta} + \left(\frac{f - \beta}{1 - \beta}\right) \ln C_i^{*c} \quad f \geq \beta \quad (7b)$$

In Eqs. (7a) and (7b), β is the volume fraction of ethanol in the aqueous phase coinciding with the breakpoint between the two segments of the model, and $C_i^{*\beta}$ is the solubility of i in the cosolvent mixture at this ethanol volume fraction.

Because of the relatively small enhancement at low cosolvent volume fractions and the relatively narrow cosolvent range (0 to ~ 0.2), solubility enhancement predicted by Eq. (7a) may also be as effectively modeled with log-linear model. This was demonstrated by Kimble and Chin (1994) for polycyclic aromatic hydrocarbons in a methanol–water binary solvent. Rather than model two different solubility mechanisms, the authors treated solubility enhancement as a piecewise two-part log-linear model incorporating two different values of the cosolubility factor, σ_i , for low and high

methanol volume fractions. Semi-logarithmic plots of measured solubility vs. methanol volume fraction for low methanol fractions showed good agreement with the log-linear behavior in that range.

2.1.3. Application to multicomponent organic phases

The log-linear cosolubility relationship (Eqs. (4) and (5)) has been used to describe equilibrium distributions in relatively simple 3-component environmental systems (e.g., Pinal et al., 1990; Barker et al., 1991). Li and Andren (1995) used a two-part equation similar to Eqs. (7a) and (7b) to model the equilibrium concentrations of individual PCB congeners in water–alcohol cosolvent systems. However, neither of these approaches have been adequately extended to complex multicomponent systems of environmental interest.

In the absence of a cosolvent, Raoult's law (Eq. (3)) is generally used to incorporate the impact of a multicomponent organic mixture on the equilibrium concentration of a species in water. Or, in the more general case, eliminating assumptions regarding ideal solution behavior in the organic phase, the organic phase activity coefficient, γ_i^o , can be included as in Eq. (2). Extending this concept to the estimation of HOC concentrations in a water–cosolvent solution in equilibrium with a multicomponent organic phase, the following expressions may be substituted for constants in the log-linear (Eq. (5)) and linear/log-linear (Eqs. (7a) and (7b)) models:

$$C_i^w = C_i^{*w} X_i^o \gamma_i^o \quad (8a)$$

$$C_i^\beta = C_i^{*\beta} X_i^o \gamma_i^o \quad (8b)$$

Because gasoline is infinitely soluble in pure ethanol, the expression for C_i^{*c} is estimated as:

$$C_i^c = \frac{X_i^o MW_i}{V^o} = \rho_i f_i^o = C_i^{*c} f_i^o \quad (8c)$$

The superscript $*$ refers to the solubilities of pure species i in pure water (w), cosolvent (c) and within the hydration spheres (β) and ρ_i is the mass density of pure compound i . Note that the first two expressions resemble Raoult's law (Eq. (3)) with the exception that γ_i^o is no longer assumed to equal unity. In Eq. (8c), V^o is the molar volume of the organic phase and f_i^o is the organic-phase volume fraction of i . This equation considers the special case where the organic phase compounds are all infinitely soluble in the cosolvent. The expression for C_i^c represents the upper bound of the equilibrium concentration, or the concentration of i for the case where the cosolvent is infinitely dilute. Where the organic phase contains only a single HOC, then $f_i^o = 1$ and $C_i^c = C_i^{*c} = \rho_i$. Substituting Eqs. (8a), (8b) and (8c) into Eqs. (5), (7a) and (7b) yields expressions for the linear and linear/log-linear models extended to multicomponent organic solutions such as gasoline.

Log-linear model:

$$\ln C_i^m = (1-f) \ln (C_i^{*w} X_i^o \gamma_i^o) + f \ln (C_i^{*c} f_i^o) \quad (9)$$

Linear/log-linear model:

$$C_i^m = \left(1 - \frac{f}{\beta}\right) C_i^{*w} X_i^o \gamma_i^o + \frac{f}{\beta} C_i^{*\beta} X_i^o \gamma_i^o \quad f < \beta \quad (10a)$$

$$\ln C_i^m = \left(1 - \frac{f - \beta}{1 - \beta}\right) \ln(C_i^{*\beta} X_i^o \gamma_i^o) + \left(\frac{f - \beta}{1 - \beta}\right) \ln(C_i^{*c} f_i^o) \quad f \geq \beta \quad (10b)$$

Eqs. (9), (10a) and (10b) may be normalized to the organic-phase composition by writing them in terms of a partition coefficient, expressed herein as the ratio between the equilibrium concentration of the HOC in an aqueous solvent and its organic-phase mole fraction, or C_i^m/X_i^o . By normalizing the aqueous concentration to organic-phase mole fractions, these alternate expressions provide a more effective method for comparing data obtained for gasolines having different formulations.

Log-linear model:

$$\ln \frac{C_i^m}{X_i^o} = (1 - f) \ln(C_i^{*w} \gamma_i^o) + f \ln\left(C_i^{*c} \frac{f_i^o}{X_i^o}\right) \quad (11)$$

Linear/log-linear model:

$$\frac{C_i^m}{X_i^o} = \left(1 - \frac{f}{\beta}\right) C_i^{*w} \gamma_i^o + \frac{f}{\beta} C_i^{*\beta} \gamma_i^o \quad f < \beta \quad (12a)$$

$$\ln \frac{C_i^m}{X_i^o} = \left(1 - \frac{f - \beta}{1 - \beta}\right) \ln(C_i^{*\beta} \gamma_i^o) + \left(\frac{f - \beta}{1 - \beta}\right) \ln\left(C_i^{*c} \frac{f_i^o}{X_i^o}\right) \quad f \geq \beta \quad (12b)$$

Note that γ_i^o is composition dependent. If the gasoline is assumed to follow thermodynamically ideal behavior, the organic phase activity coefficients become unity and γ_i^o drops out of Eqs. (11), (12a) and (12b). For standard-formulation gasolines, where oxygenates are absent, this assumption is commonly employed. The errors imposed by these assumptions are addressed in Section 4 of this paper.

2.2. UNIFAC model

An alternative approach to computing the equilibrium HOC concentrations in an aqueous cosolvent mixture is to solve Eqs. (1a) and (1b) for each component i subject to a mass-balance constraint:

$$n_i^w + n_i^o = n_i^{w+o} \quad i = 1 \dots n \quad (13)$$

where n_i^j defines the number of moles of compound i in phase j and $w + o$ represents the combined aqueous and organic phases (Sorensen et al., 1979). Solving the $2n$ equations yields the number of moles of each component in each of the two phases that can then be converted to units of mass concentration.

The activity coefficients for each phase in Eqs. (1a) and (1b) are computed using a thermodynamic model relating activity coefficients to the composition of the given phase. Most models for estimating activity coefficients (i.e., Margules, UNIQUAC, and NRTL) require a substantial amount of experimental data to fit the model parameters

(Smith and Van Ness, 1987). Of these, the UNIQUAC (universal quasi chemical) model (Abrams and Prausnitz, 1975) is often used in multicomponent liquid–liquid equilibrium problems. This model utilizes statistical mechanics to include the effect of molecular structure on liquid activity coefficients, resulting in a basic equation that incorporates the influence of both the entropy effects associated with the size and shape of a molecule (the combinatorial part) and the molecular interactions of functional groups between the different molecules (the residual part) (Henley and Seader, 1981). The UNIFAC (*UNIQUAC functional-group activity coefficients*) model, was developed with the same theoretical basis as UNIQUAC, although, necessary parameters are estimated from the number and type of functional groups that comprise the chemical species. Since this model does not require extensive data, it is more easily implemented than UNIQUAC, although additional errors are introduced by estimating rather than measuring some of the parameters. UNIFAC is based on the premise that surface volume and area properties of the individual functional groups that comprise a molecule can be summed to estimate properties of the entire molecule (Fredenslund et al., 1975). The group parameters are tabulated for numerous functional groups in most standard thermodynamics textbooks (e.g., Smith and Van Ness, 1987). Additional parameters describing interactions among each of the functional groups are also required for the UNIFAC model. These group interaction parameters have been determined from large databases of experimental data for both vapor–liquid and liquid–liquid systems and have been updated numerous times since the initial development of the UNIFAC model.

UNIFAC has been used fairly extensively in environmental applications. Numerous researchers have used this model to estimate the aqueous phase solubility of HOCs in organic phase–water systems, both with and without cosolvents. Reasonable prediction capabilities in these 2–3 component systems—generally within a factor of two relative to experimental data—have been reported (Banerjee, 1985; Arbuckle, 1986; Fu and Luthy, 1986; Groves, 1988; Pinal et al., 1990; Mihelcic, 1990). In an effort to improve the predictive capabilities of UNIFAC for HOCs, Chen et al. (1993) evaluated a database of published aqueous phase solubilities and octanol–water partition coefficients to develop a new set of binary interaction parameters better suited for environmental applications.

Kan and Tomson (1996) recently completed a comprehensive evaluation of the applicability of UNIFAC for predicting aqueous solubilities of environmentally significant HOCs. With several different sets of published values of the vapor–liquid functional group binary interaction parameters, they found excellent agreement between experimentally measured and predicted solubilities of pure chemicals in water. In general, the predictions were within one order of magnitude of the measured solubilities with the greatest discrepancies observed for high molecular weight or chlorinated hydrocarbons. As with most other applications, the analysis of Kan and Tomson (1996) involved systems with only 2–3 components.

Hellinger and Sandler (1995) examined the ability of both UNIQUAC and UNIFAC to model their measured gasoline–water–oxygenate solubility data. They considered single alkane species as surrogates for all species in the gasoline and *t*-amyl methyl ether or *t*-amyl alcohol as the added oxygenates. Both UNIFAC and UNIQUAC provided qualitative descriptions of trends in the ternary diagrams representing equilib-

rium compositions of the two phases. However, neither was accurate in a quantitative sense, especially for the solubility of the alkane in the aqueous phase.

The difficulty in utilizing UNIFAC for more complex systems is the need to understand the composition and structure of all components within the system. This is typically not feasible with complex petroleum hydrocarbons. Perry and Chilton (1973) suggest the use of ‘pseudocomponents’ to lump many components into one with average properties. Peters and Luthy (1993) described a coal tar as a pseudocomponent in an assessment of phase equilibria for ternary coal tar–water–solvent systems. They found that this approach was useful for analyzing the effect of polar solvents added to increase coal tar solubilization.

3. Experimental methods

BTEX and ethanol partitioning relationships were established by performing batch equilibrium experiments using both simple and complex ‘gasolines.’ Experiments were first performed using three simple gasolines of variable complexity in order to ensure that the system was well characterized. Additional experiments with more complex commercial reformulated gasolines containing ethanol were performed to verify results with the surrogate-compound gasolines. Equilibrium BTEX and ethanol concentrations were measured in both phases and partition coefficients were computed as a function of the aqueous-phase ethanol volume fraction.

Surrogate-compound gasolines were incorporated into the study so that partition coefficients (C_i^m/X_i^o) could be measured using organic solutions of known composition. The complexity of these solutions was successively increased and included: (1) a single aromatic and ethanol (2-component gasoline); (2) an aromatic plus an alkane and ethanol (3-component gasoline); and, (3) the six BTEX compounds with a single alkane and ethanol (8-component gasoline). Isooctane was used as the surrogate alkane in each of these mixtures. With this series of surrogate-compound gasolines, the effects of non-ideal solution characteristics could be ascertained. Table 1 summarizes the composition of these organic mixtures. Because nearly all of the ethanol partitions into the aqueous phase, ethanol was always added to water rather than the organic solution. This resulted in minimal changes in the relative volumes of the two phases upon mixing.

The two commercial gasolines included a reformulated gasoline containing 5.8% ethanol by volume obtained directly from the Phillips Chemical and a generic gasoline, also containing ethanol, obtained from a Canadian service station. The reformulated gasoline obtained from Phillips Chemical is a certified gasoline marketed for automobile emissions testing under the California Phase II air-quality program and is herein designated as the C2 gasoline. The generic gasoline was purchased from a Gas Bar station in Cornwall, Ontario. The ethanol content in that gasoline was measured to be 3.8% by volume.

A synthetic groundwater was prepared for all experiments. The aqueous solution contained sodium chloride to raise the ionic strength to approximately 10^{-2} moles/l. In addition, sodium bicarbonate was added to provide solution buffering so that the pH would remain at a relatively constant value of 7.2. Pure ethanol was added directly to

Table 1

Starting composition of gasolines used in batch equilibrium experiments

Gasoline	Ethanol	Isooctane	Benzene	Toluene	Ethylbenzene	Total xylenes	Total BTEX
<i>Volume fraction</i>							
2-Component	Added to water ^a	—	—	—	—	1.00 ^b	1.00
3-Component	Added to water ^a	0.833	—	—	—	0.167 ^b	0.167
8-Component	Added to water ^a	0.831	0.00801	0.0584	0.0255	0.0768 ^c	0.169
Phillips C2 ^{d,e}	0.0576	0.118	0.00819	0.0611	0.0267	0.0775	0.173
Gas-Bar ^{d,e}	0.038	ND ^f	0.0077	0.034	0.012	0.045	0.099
<i>Mole fraction</i>							
2-Component	Added to water ^a	—	—	—	—	1.00	1.00
3-Component	Added to water ^a	0.788	—	—	—	0.212	0.212
8-Component	Added to water ^a	0.774	0.0138	0.0845	0.0320	0.0960	0.226
Phillips C2 ^{d,e}	0.126	0.0918	0.0118	0.0737	0.0279	0.0807	0.194
Gas-Bar ^{d,e}	0.098	ND ^f	0.013	0.049	0.015	0.056	0.13

^aFor convenience, ethanol was initially added to water rather than gasoline.^b*m*-Xylene.^cIncludes the three isomers of xylene in approximately equal fractions.^dDetermined by GC.^eCompounds in gasoline that were not quantified are assumed to have an average molecular weight of 100 g/mole.^fND-not determined.

the water to make cosolvent solutions containing ethanol mass fractions ranging between 0 and 70%. Ethanol contents were measured for each aqueous solution by weighing water and then re-weighing the ethanol–water solution following the addition of ethanol.

For the batch equilibrium tests, the synthetic groundwater containing a range of ethanol volume fractions was contacted with a gasoline in specially-constructed glass vials. Teflon-lined septa at both ends allowed syringe sampling of both the aqueous and organic phases while preventing contact of the syringe needle with the adjoining phase. The volume of the vials ranged between 64 and 77 ml.

For all but a few tests, the mixtures were prepared by first filling 50% of the vial with the ethanol–water solution. The remaining volume was then filled with the organic solution. For several experiments involving the C2 and Gas-Bar gasolines, the vial was initially filled with as much as 70% water in order to attain an aqueous phase with a very low ethanol fraction. Immediately after the organic solution was added, the upper septum was put in place allowing a small quantity of the organic solution to overflow in order to minimize the amount of air in the vial. Following the addition of each phase, the vial and its contents were weighed for more precise measurement of the materials added. The vials were then rotated for a minimum equilibration time of 24 h at a constant temperature of 20°C using a Roto-Torque rotator (Cole–Parmer, model 7637). The 24-h period was deemed sufficient following the completion of exploratory experiments performed for variable equilibration times which showed little variation in solubility behavior for equilibration periods longer than several hours.

Following the equilibration period the contents were sampled. The aqueous phase was first sampled using a glass Hamilton Gastight 5-ml syringe to penetrate the lower septum and extract a portion of the aqueous phase. The equilibration of pressure with the atmosphere was maintained by placing a syringe needle in the opposite septum to serve as a vent. The aqueous sample was then dispensed into duplicate 2-ml autosampler vials. Subsequently, a sample of the organic phase was similarly extracted through the upper septum of the vial using a separate 5-ml syringe and placed into duplicate autosampler vials.

The concentrations of the BTEX compounds and ethanol were measured using a Hewlett Packard model 5890 gas chromatograph (GC) fitted with a Supelco (model 9071-03) capillary column and a Hewlett Packard flame ionization detector. Calibration standards containing known amounts of ethanol and BTEX compounds in both water and isooctane were prepared in the laboratory and were analyzed immediately prior to measuring the batch samples. For each phase, as few as four, but generally six standards were prepared and analyzed to establish linear calibration curves for the BTEX and alkane compounds and quadratic curves for ethanol. The calibration curves consistently yielded r^2 values greater than 0.99. Both standards and the samples were analyzed in duplicate and the measured concentrations were averaged. As a measure of precision of the GC analyses, a relative range for each duplicate pair was calculated by dividing the difference between the high and low values by the average of the pair. The median of the relative range of duplicates ranged between 1% and 3% for aqueous-phase samples and 0.4% and 0.8% for organic-phase samples. Densities of the aqueous and organic phase samples were measured at 20°C using pycnometers to convert volumes of sample injected into the GC to units of mass.

4. Experimental results and discussion

Results of batch equilibrium tests are first presented for xylene. By initially focusing on a single BTEX compound, the effects of the aqueous-phase ethanol content and organic-phase composition can be better evaluated. Subsequently, the xylene behavior is compared with that of other BTEX compounds in order to evaluate how the individual BTEX compounds are affected by cosolvency.

4.1. Xylene partitioning

The xylene partition coefficients are shown in Fig. 1. Partition coefficients, computed by dividing measured aqueous phase xylene concentrations by the measured organic phase xylene mole fractions, are presented in order to compare experimental data directly without influence of the organic phase composition. Hence, even though the aqueous phase concentrations were measured using surrogate gasolines with xylene mole fractions ranging from approximately 0.05 to 1.0, the partition coefficients display similar values. Aqueous ethanol contents are expressed in units of volume fraction.

The three sets of data illustrating the relationship between partition coefficient and aqueous phase ethanol volume fraction all display an approximate linear trend at ethanol

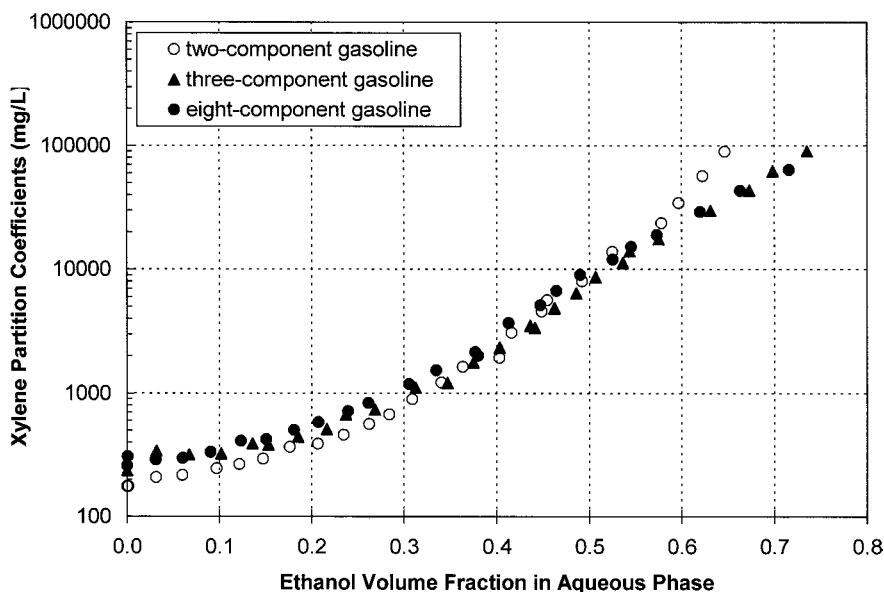


Fig. 1. Xylene partition coefficients (C_i^m / X_i^o) measured for three surrogate gasolines.

volume fractions greater than approximately 0.2 when plotted on semi-log scale. At lower concentrations, however, there is a distinctly different trend that appears to be consistent with the observations of Banerjee and Yalkowsky (1988).

4.2. Benzene, toluene and ethylbenzene partitioning

Measured partition coefficients for the suite of BTEX species in the 8-component gasoline are presented on Fig. 2. As with xylene, a distinct difference in the extent of cosolvency—represented by the slopes of the curves—is evident between low ($f < \sim 0.20$) and high volume fractions of the cosolvent. The cosolvency effect is also dependent on the hydrophobicity of the solute with the greatest increase in partition coefficient as a function of ethanol volume fraction measured for the most hydrophobic compound, xylene. This relationship between cosolvency and hydrophobicity is predicted by Eqs. (11), (12a) and (12b) and has been observed by others (e.g., Munz and Roberts, 1986).

4.3. Ethanol partitioning

Because it is the ethanol content in the aqueous phase rather than the organic-phase that most impacts BTEX solubility, the partitioning of ethanol between phases must also be considered. Ethanol partition coefficients for the three surrogate-compound gasolines are shown on Fig. 3 as a function of the aqueous-phase ethanol content. Ethanol partition coefficients are expressed as ratios of volume fractions to be consistent with the dimension used for the aqueous-phase ethanol content. Partition coefficients for a

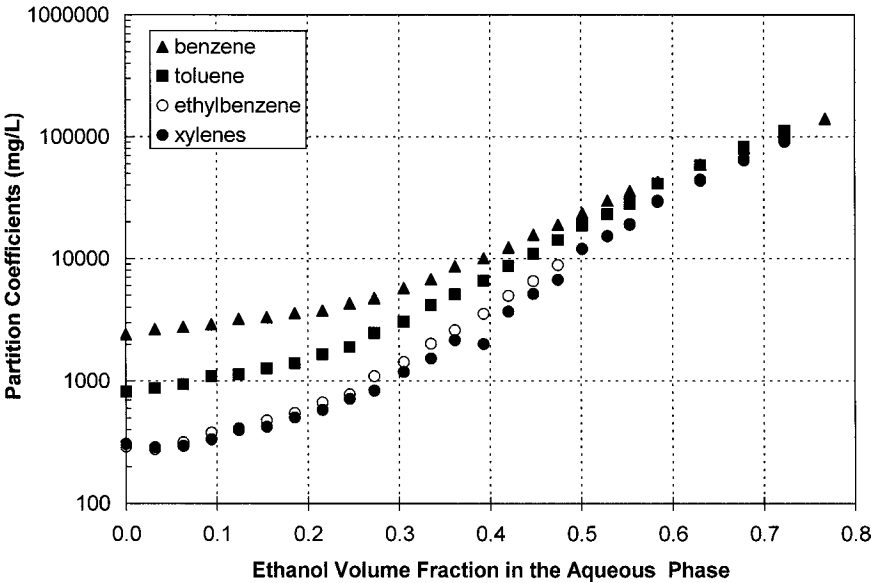


Fig. 2. BTEX partition coefficients (C_i^m / X_i^o) measured for 8-component gasoline.

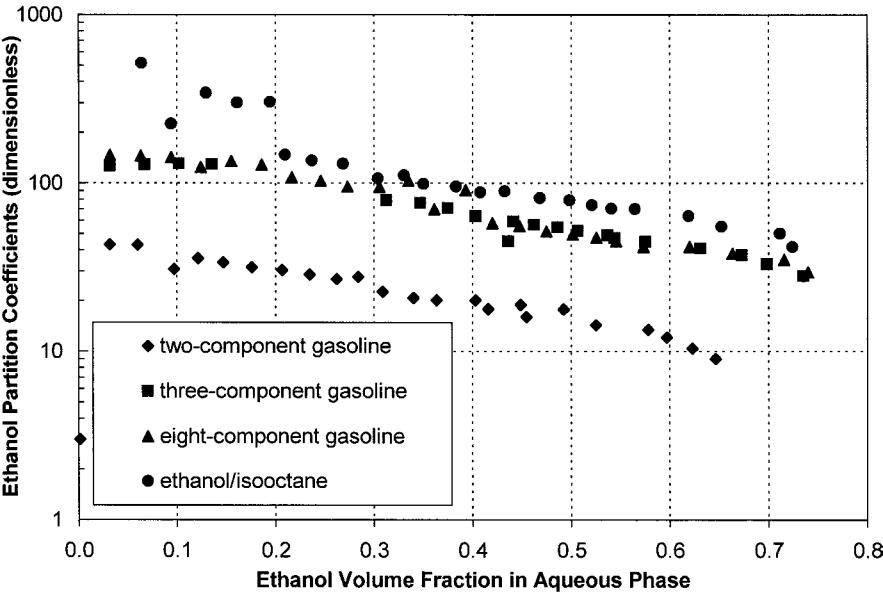


Fig. 3. Ethanol partition coefficients (f/f^o) measured for several surrogate gasolines.

mixture of isooctane, ethanol and water are also included on this figure to evaluate the effect of the alkanes on ethanol partitioning. These data demonstrate that ethanol partitions with strong preference into the aqueous phase. For example, if equal volumes of water and gasoline containing 10% ethanol are equilibrated, more than 99% of the ethanol will partition into the aqueous phase.

For all surrogate gasoline mixtures, ethanol partition coefficients decrease with increasing aqueous ethanol content. This change occurs in an approximate log-linear manner. The preferential partitioning of ethanol into the aqueous phase is much greater for the more hydrophobic alkanes and mixtures of aromatics and alkanes than for pure xylene. Partitioning behavior observed for the 3- and 8-component mixtures is nearly identical indicating little or no effect of composition within the aromatic portion of the gasoline on ethanol partitioning.

4.4. Non-ideal solution behavior in the organic phase

Data presented in Fig. 1 indicate some discrepancies in the partition coefficient as the ethanol volume fraction approaches zero. The xylene partition coefficients measured using the 2-component gasoline approach 180 mg/l while partition coefficients measured using the 3-component and 8-component gasolines approach approximately 240 mg/l and 260 mg/l, respectively (Fig. 1). For the 2-component gasoline, the xylene mole fraction approaches unity under these limiting conditions and the equilibrium established is between pure xylene and water. In this case, the measured partition coefficient matches published aqueous solubility values for xylene (Vershueren, 1983). Under the assumption of ideal-solution interactions in the gasoline, the application of Raoult's law (Eq. (3)) for the multicomponent mixtures, would predict the partition coefficients for all three gasoline formulations to be equal. Partition coefficients for xylene in the multicomponent mixtures were, however, significantly greater than predicted by this approach. Similarly, the benzene, toluene and ethylbenzene partition coefficients (Fig. 2) consistently exceed the values predicted by Raoult's Law (Eq. (3)) incorporating the measured mole fractions and published C_i^{*w} values (Vershueren, 1983).

These discrepancies are attributed to non-ideal interactions between the BTEX compounds and isooctane in the organic phase resulting in organic-phase activity coefficients that exceed unity. This contradicts traditional assumptions of ideal behavior in standard-formulation gasolines as reflected by Raoult's law. However, evidence supporting these non-ideal interactions between BTEX compounds and alkanes is presented in Fig. 4, which shows activity coefficients for benzene, toluene and *p*-xylene each in solution with heptane. The activity coefficients were calculated from vapor–liquid equilibrium measurements at 25°C compiled by Gmehling et al. (1980, 1983). The figure shows activity coefficients exceeding unity by as much as a factor of 1.5 for all three BTEX compounds in solution with an alkane. At a BTEX volume fraction of 17%—equal to that of *m*-xylene in the three component gasoline—the activity coefficients of the three BTEX compounds shown in Fig. 4 range approximately between 1.3 and 1.4. Fig. 4 also shows UNIFAC estimates of activity coefficient for xylene in a xylene–isooctane binary mixture. The UNIFAC predictions agree well with the activity coefficients calculated from vapor–liquid equilibria data.

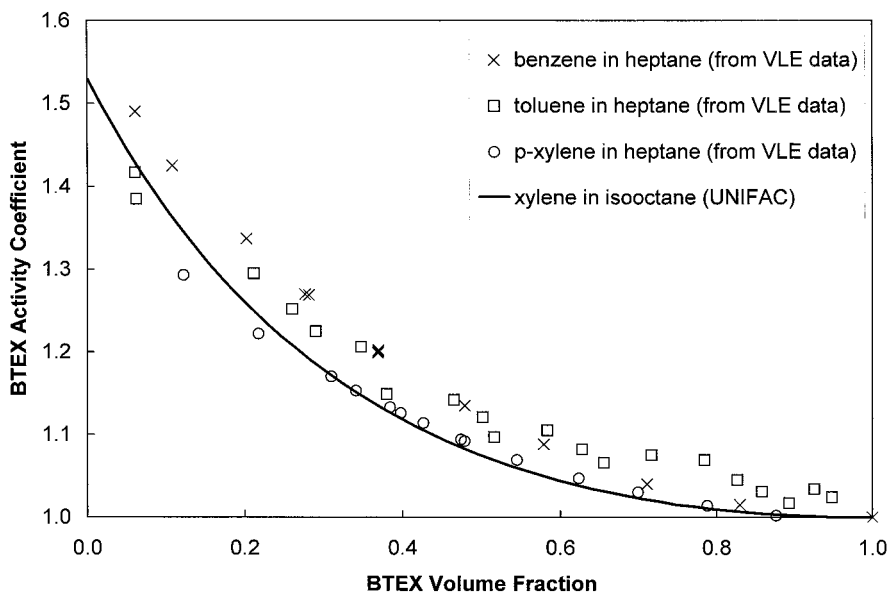


Fig. 4. Measured activity coefficients for benzene, toluene and xylene in heptane at 25°C and UNIFAC-generated activity coefficients for xylene in isooctane and in an isooctane–BTEX solution.

Organic-phase activity coefficients can be estimated from the batch-equilibrium data for the 3- and 8-component gasolines by rearranging Eq. (8a). For the case of no ethanol ($f = 0$),

$$\gamma_i^o = \frac{C_i^w/X_i^o}{C_i^{*w}} \quad (14)$$

Substituting the partition coefficients measured using the 3-component gasoline ($C_i^w/X_i^o = 240 \text{ mg/l}$) and the 2-component gasoline ($C_i^{*w} = 180 \text{ mg/l}$) into Eq. (14) yields an activity coefficient of 1.3, which is within the range of values shown on Fig. 4 for 17% BTEX in heptane.

For the case when ethanol is present in the water–gasoline system, organic-phase BTEX activity coefficients are not expected to significantly change. This is indicated from vapor–liquid equilibrium measurements performed for an ethanol–benzene–heptane system (Gmehling and Onken, 1977) which show that the presence of ethanol in the organic phase at fractions less than 10% alters the BTEX activity coefficients by less than 5%. A gasoline in equilibrium with water is expected to have ethanol concentrations much lower than 10% due to the highly preferential partitioning of ethanol into the aqueous phase.

5. Mathematical modeling

The three mathematical models identified in Eq. (2) were applied to experimental data presented above for the 8-component surrogate-gasoline mixture. The log-linear

(Eq. (11)) and UNIFAC models were used in a predictive capacity while some fitting of parameter values was required for application of the linear/log-linear model (Eqs. (12a) and (12b)). All of the models were then used to predict aqueous phase concentrations for the Philips C2 and Gas Bar reformulated gasolines for comparison of model estimates to experimental measurements. In addition, solubility data collected by other researchers for a Brazilian gasoline (Fernandes, 1997) were considered in the assessment of the predictive capacity of the models.

5.1. Model application

The log-linear model can be used in a predictive mode when solubilities of the pure species i in each of the two pure solvents are known. The solubilities of each compound in pure water were obtained through literature sources (Vershueren, 1983) (Table 2). It was assumed that the organic-phase behaves ideally ($\gamma_i^o = 1$) in order that this model be applied in a predictive manner and in its most easily used form.

Application of the linear/log-linear model (Eqs. (12a) and (12b)) requires, a minimum of three parameters to be determined empirically. These parameters, which include the ethanol volume fraction, β , at the breakpoint between the two sections of the model; the quantity $C_i^* \beta \gamma_i^o = \beta$ at $f = \beta$; and the organic-phase activity coefficient, γ_i^o at $f = 0$, were determined by fitting Eqs. (12a) and (12b) to the 8-component gasoline experiments. Preliminary regression analyses with these three fitting parameters indicated a distinct departure of the model from the 8-component data at high ethanol fractions. Thus a fourth parameter, the quantity $(C_i^* f_i^o / X_i^o)$ was also fit to the data rather than calculated from known values of each term. As with the log-linear model, the solubilities of the BTEX compounds in pure water were obtained from the literature (Vershueren, 1983). The statistical package SYSTAT was used to perform a non-linear piecewise least-squares regression.

Application of the UNIFAC model required the solution of a system of equations Eqs. (1a), (1b) and (13) while incorporating the UNIFAC equations to compute the activity coefficients required by Eqs. (1a) and (1b). Specified parameters included the total composition of the combined phases, n_i^{w+o} , the temperature and an initial estimate of the distribution of the total number of moles between phases. The model output consisted of the number of moles of each compound in each of the two phases.

A FORTRAN computer code adapted from Prausnitz et al. (1980) was written utilizing method of Rachford and Rice (Prausnitz et al., 1980) to solve the system of equations in conjunction with a Pickard iteration to update and refine the activity coefficients. Binary interaction parameters published by Hansen et al. (1991) for vapor–liquid equilibria, Magnussen et al. (1981) for liquid–liquid equilibria, and Chen et al. (1993) for environmentally significant HOCs were considered in an earlier phase of this work. The parameters developed for vapor–liquid equilibria (Hansen et al., 1991) were found to provide the most accurate prediction of experimental data describing the partitioning of BTEX between reformulated gasolines and water (Heermann and Powers, 1997), and are used here.

Partition coefficients resulting from the application of the three mathematical models are shown along with measured values on Fig. 5. Parameters determined from fitting the

Table 2
Parameters for log-linear (Eq. (11)) and linear/log-linear equations (Eqs. (12a) and (12b)) for 8-component surrogate gasoline

Component	Log-linear model		Linear/log-linear model			
	C_i^{*w} (mg/l) ^a	$C_i^{*c} f_i^o / X_i^o$ (mg/l) ^b	γ_i^o (at $f=0$) ^c	$C_i^{* \beta} \gamma_i^o$ (mg/l) ^c	β (–) ^c	$C_i^{*c} f_i^o / X_i^o$ (mg/l) ^c
Benzene	1780	508,000	1.41 (±0.09)	4420 (±340)	0.270 (±0.015)	963,000 (±111,000)
Toluene	515	600,000	1.51 (±0.13)	1360 (±150)	0.226 (±0.017)	1,040,000 (±137,000)
Ethylbenzene	152	698,000	1.72 (±0.21)	450 (±40)	0.203 (±0.021)	1,265,000 (±218,000)
Xylenes	~ 180	685,000	1.48 (±0.21)	473 (±92)	0.204 (±0.025)	1,164,000 (±231,000)

^aFrom Vershueren (1983).

^bComputed using C_i^{*c} from Vershueren (1983), and f_i^o and X_i^o from Table 1 (Eq. (8c)).

^cParameter estimate (±95% confidence interval).

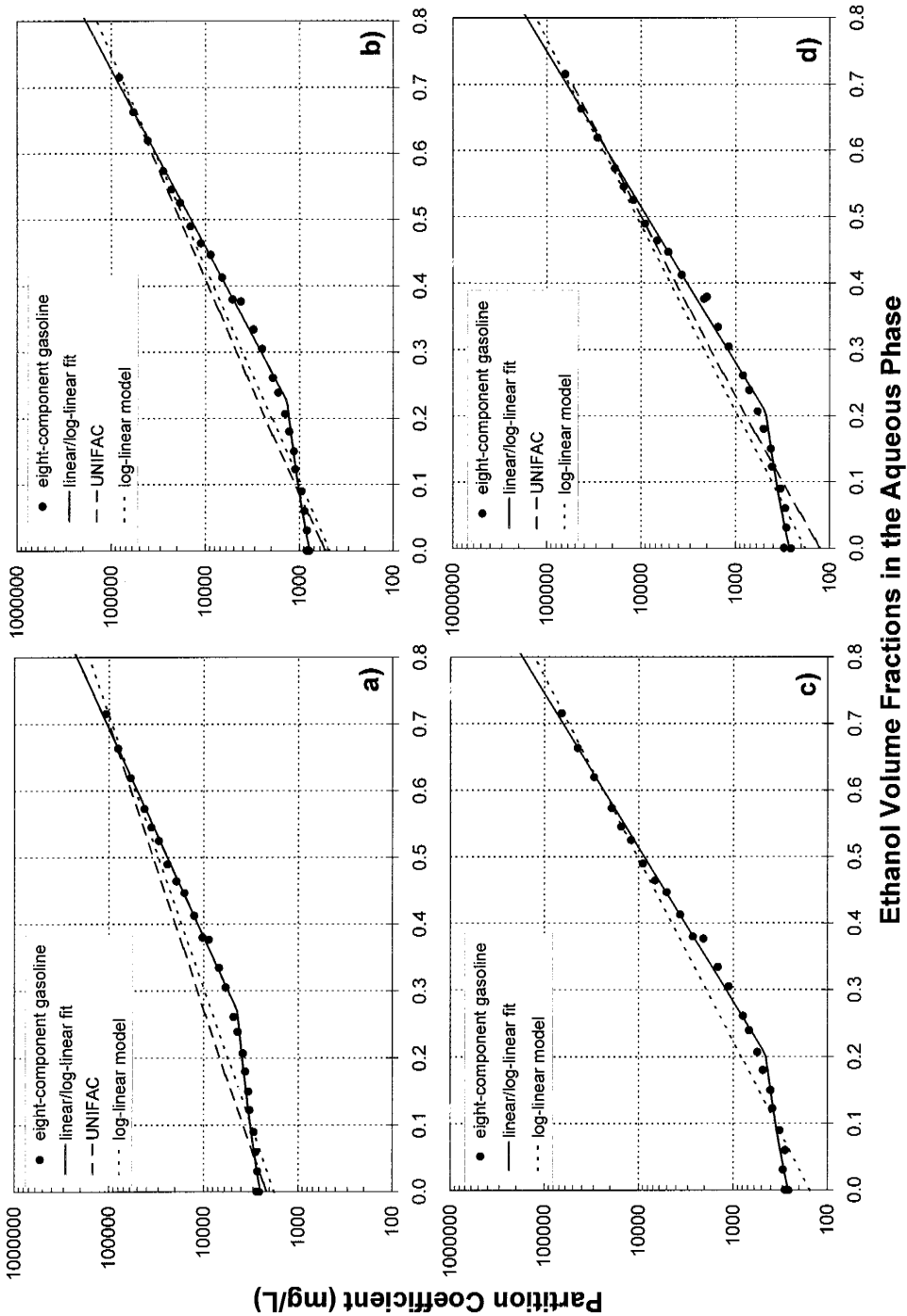
linear/log-linear model equations to these data are provided in Table 2. Comparison of the UNIFAC and log-linear model predictions to the measured partition coefficients indicates that both predict the general increase in partition coefficients as the volume fraction of ethanol is increased. However, because neither of these models accounts for the differences in solubilization mechanisms between the low and high ethanol fractions, there are deviations on the order of a factor of two. The greatest differences occur approximately at the ethanol volume fraction coinciding with the observed slope change.

The improved fit of the linear/log-linear model supports the observations of Banerjee and Yalkowsky (1988) that solubility is affected differently at low aqueous cosolvent fractions than at fractions above a certain value, β . By fitting γ_i° (Table 2), non-ideal interactions between the alkane and aromatic species in the organic phase are incorporated into the model. Fitted values of γ_i° are generally within the range shown on Fig. 4. Thus, with the incorporation of non-ideal solution characteristics and the different mechanisms of solubilization between high and low ethanol volume fractions, Eqs. (12a) and (12b) provides the most accurate description of data. Unlike the UNIFAC and log-linear models, however, parameter values had to be determined from experimental measurements. The fitted values of C_i^c are approximately 70–90% higher than would be predicted from Eq. (8c). This discrepancy may arise from a departure from log-linear behavior at high ethanol fractions. Alternatively, the discrepancy may result from the formation of a single phase at an ethanol fraction less than unity. Neither of these alternative hypothesis was investigated as part of this study.

An apparent weakness of the linear/log-linear model is suggested by a variation in fitted β values for different solutes in excess of the confidence intervals. Table 2 shows an apparent decrease in β values with increasing solute hydrophobicity. Even greater variation is indicated by solubility data published by Rubino and Yalkowsky (1987) which show a maximum departure from log-linear behavior at a volume fraction of 0.6 for three pharmaceutical drugs in an ethanol–water binary solvent. This implies a breakpoint significantly different to that measured herein for the BTEX compounds. Another approach for estimating β , based on the theoretical volume of the hydration spheres formed when ethanol is added to water (145 ml per mole of ethanol) (Grunwald, 1984) resulted in an estimate of 0.4, which is also significantly higher than the values shown on Table 2. Additional experiments performed over a larger range of solute hydrophobicities would be necessary to assess any dependence of β on the solute properties and provide a means of predicting the value of this parameter.

5.2. Model prediction

From a practical standpoint, the primary benefit of a model that can quantify the partitioning of contaminants from reformulated gasoline is the ability to predict concentrations of BTEX in groundwater or surface water contaminated with these gasolines. These equilibrium calculations often form the basis of preliminary exposure and risk assessments and solute transport modeling efforts. Application of these models requires assumed values for the equilibrated volume ratio of gasoline to water, as well as the composition of the gasoline. Typically, BTEX concentrations in gasoline can be measured, but the overall composition of gasolines cannot be fully quantified. Thus, in



any application of gasoline partition equations, a suitable approximation of the composition of this unknown fraction is required to convert measured BTEX concentrations to the mole fractions required by UNIFAC or the linear/log-linear model.

The linear/log-linear and UNIFAC models were used to predict BTEX concentrations in the aqueous phase equilibrated with three commercial reformulated gasolines. A surrogate 'pseudocomponent' was used in both models to represent all of the unknown alkane, alkene, and cycloalkane species. Several representative compounds found in gasoline were considered. Ideally, the properties of a gasoline approximated with a pseudocomponent should have similar properties as a standard gasoline. For comparison, the density and molecular weight of the C2 gasoline calculated with a pseudocomponent to represent all unknown species were compared to the density (0.73 g/ml) and molecular weight (96 g/mol) of the API standard PS-6 gasoline (Barker et al., 1991). The use of heptane as a pseudocomponent provided the closest estimation of these properties and was used in the model predictions described here.

Aqueous BTEX concentrations in equilibrium with the commercial gasolines were predicted using the linear/log-linear model (Eqs. (12a) and (12b)) utilizing parameters determined from fitting this model to the 8-component surrogate gasoline experimental data (Table 2). Because the equilibrium volume fraction of ethanol in the aqueous phase is the independent variable in Eqs. (12a) and (12b), this variable had to be estimated prior to predicting the BTEX concentrations. Based on the experimental results described in Section 4.3, it was assumed that 100% of ethanol in the gasoline partitions into the aqueous phase. Thus, from a mass balance on the system, the volume fraction of ethanol in the aqueous phase can be estimated as:

$$f = \left[\frac{\frac{V^o}{V_w} f_{in}^o \rho_{et}}{\frac{V^o}{V_w} f_{in}^o \rho_{et} + \rho_w} \right] \frac{\rho^m}{\rho_{et}} \quad (15)$$

where V^j is the initial volume of gasoline (o) or water (w); f_{in}^o is the initial volume fraction of ethanol in the gasoline, ρ_j is the density of pure ethanol (et) and water (w), and ρ^m is the density of the cosolvent mixture at equilibrium. The density of the cosolvent mixture can be estimated with a polynomial curve fit to data (Perry and Chilton, 1973) describing the nonlinear nature of the density of ethanol–water mixtures:

$$\rho^m = 0.0967W_{et}^4 - 0.1690W_{et}^3 + 0.0023W_{et}^2 - 0.1351W_{et} + 0.9982 \quad (16)$$

where W_{et} is given by the quantity in brackets in Eq. (15). Errors in estimates of f resulting from the assumption of 100% ethanol partitioning into the aqueous phase are as high as 10%. The greatest errors occur at high ethanol fractions in the C2 gasoline. The propagation of these errors in the estimation of BTEX concentrations is discussed below.

Fig. 5. Mathematical models describing partitioning behavior of eight-component gasoline: (a) benzene, (b) toluene, (c) ethylbenzene and (d) xylenes. (Note: due to a limit of six species in the UNIFAC model employed here, simulations with this model were not completed for ethylbenzene.)

Table 3

Quality of the predictions of aqueous phase compositions equilibrated with the real gasolines

Compound	Phillips C2		Gas-Bar		Brazilian	
	UNIFAC	Linear/log-linear	UNIFAC	Linear/log-linear	UNIFAC	Linear/log-linear
<i>Mean-square error^a</i>						
Benzene	0.064	0.019	0.100	0.034	0.007	0.064
Toluene	0.040	0.013	0.075	0.030	0.010	0.012
Xylenes	0.021	0.014	0.053	0.034	0.019	0.016
<i>Maximum % error^b</i>						
Benzene	140	65	181	65	103	101
Toluene	112	50	155	76	60	47
Xylenes	86	54	127	89	38	56

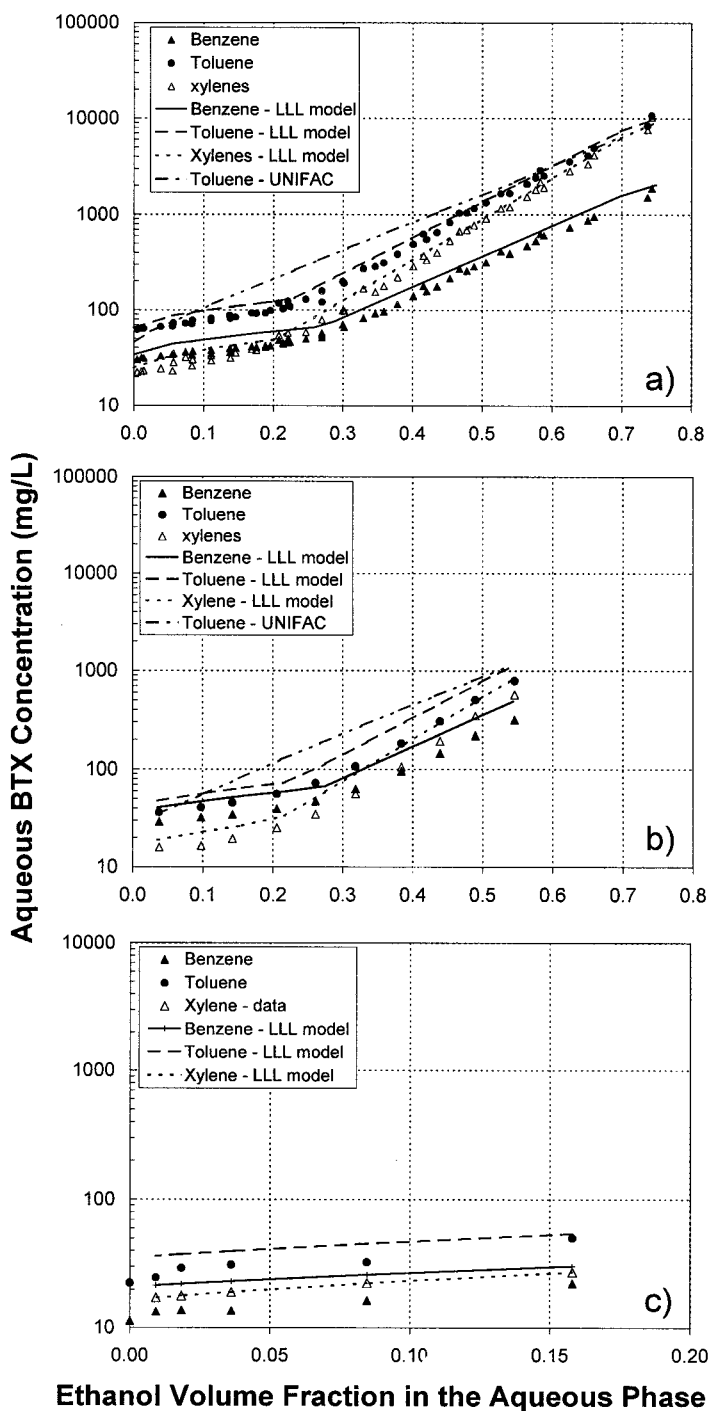
^aMean-square error = $1/n \sum_i (\ln C_{\text{meas}_i} - \ln C_{\text{pred}_i})^2$.^bMaximum % error = $\max[100((C_{\text{meas}_i} - C_{\text{pred}_i})/C_{\text{meas}_i})]$.

Equilibrium mole fractions of the BTEX species in the organic phase are also required to estimate aqueous phase concentrations from partition coefficient equations. Experimental results showed that minimal mass of BTEX was depleted from the gasoline as it equilibrated with the aqueous phase. Thus, the mole fractions were estimated based on the original composition of the gasoline with an adjustment for the loss of ethanol. The assumptions regarding the organic phase composition and the ethanol content in the cosolvent mixture both result in overestimates of BTEX concentrations in the aqueous phase.

The capability of the linear/log-linear and UNIFAC models to predict measured concentrations of benzene, toluene, and xylenes (BTX) in each of the batch equilibrium experiments with the C2 and Gas Bar gasolines is quantified in Table 3 with representative data presented in Fig. 6. The errors presented in Table 3 were calculated as both the maximum % error between measured and predicted concentrations for any datum and the mean squared error calculated from the logarithm of the concentrations as a measure of the overall quality of the prediction. Additional data collected by Fernandes (1997) for a Brazilian commercial gasoline containing 22% ethanol by volume are also included. It should be noted that the experiments performed using the Brazilian gasoline were performed independently by others with different procedures from those described earlier.

The linear/log-linear model performs well in predicting the general trends in measured concentration data. BTX concentrations predicted with the linear/log-linear model are consistently higher than measured, although they rarely exceed measured values by more than 50%. A portion of this discrepancy is attributed to overestimates of the aqueous ethanol volume fraction. Consequently, the error could be reduced with a more sophisticated ethanol partitioning algorithm.

Fig. 6. Mathematical model predictions of the concentrations of benzene, toluene, and xylenes in the aqueous phase equilibrated with (a) C2, (b) Gas Bar, and (c) Brazilian reformulated gasolines.



There are somewhat greater deviations between the linear/log-linear model predictions for benzene concentrations resulting from exposure to the Brazilian gasoline, although all predicted concentrations are still within a factor of two (Table 3, Fig. 6). Differences between the experimental and predicted concentrations can typically be described as error in the intercept of the curve, not the slope which would likely result from erroneous estimates of BTX mole fractions for the organic phase.

As expected, UNIFAC only predicts a general log-linear relationship between concentrations and ethanol volume fractions over the entire range of volume fractions (Fig. 6). Thus, even though the model predictions are consistent at the high and low extremes, BTX concentrations are overestimated in most cases. Maximum errors on the order of 50–200% occur in the vicinity of $f = \beta$.

Comparison of the mean-square error (MSE) and maximum % error for the linear/log-linear and UNIFAC predictions for the three commercial gasolines (Table 3) shows that the linear/log-linear predicted aqueous BTX concentrations with a greater degree of accuracy. This implies that the model parameters computed from 8-component gasoline (Table 3) may be applied to other commercial gasolines. However, these parameters were measured using a single BTEX:alkane ratio and so caution should be pursued when extrapolating these parameters to gasolines with significantly different aromatic:aliphatic hydrocarbon ratios. The organic-phase activity coefficients are highly sensitive to this ratio (Fig. 4).

6. Conclusions

Experimental measurements were conducted to quantify the extent of BTEX partitioning from reformulated gasolines containing ethanol. The results of these experiments, expressed as partition coefficients as a function of the ethanol volume fraction in the aqueous phase, display an approximate linear trend when plotted on semi-log scale at ethanol volume fractions greater than approximately 0.2. At lower concentrations, however, a distinctly different trend was observed. Expressing the data as partition coefficients rather than aqueous phase concentrations provided a means of normalizing the results such that they are independent of the gasoline composition. Slight deviations in the partition coefficients (20–40%) were observed among the different surrogate gasolines, especially at low ethanol concentrations due to non-ideal interactions between alkane and aromatic compounds within the gasoline. Because of these interactions, it was found that surrogate gasolines comprised of both alkanes and aromatics provided better representation of real gasolines than pure aromatic species.

Three mathematical models were applied to the experimental results. The log-linear and UNIFAC models were applied in a predictive capacity. They were capable of representing the overall increase in aqueous-phase BTX concentrations as a function of increasing ethanol content. However, neither of them mimicked the observed two-part curve. A piecewise model comprised of a linear relationship for low ethanol volume fractions and a log-linear model for higher concentrations was fit to data for a surrogate gasoline comprised of eight compounds. These parameters were then used to predict BTEX concentrations in the aqueous phase equilibrated with three different commercial

gasolines containing ethanol. This model was superior to the UNIFAC predictions, especially at the low ethanol concentrations expected when gasolines presently sold are spilled in the environment. Thus, the linear/log-linear model parameters presented here can be utilized to predict groundwater contamination by gasolines containing ethanol when the relative volumes of the two phases and the gasoline composition can be estimated.

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